

Showcasing research from Pengqiang Yan and Prof. Wei Qi at the Institute of Metal Research, Chinese Academy of Sciences, China.

Methanol oxidative dehydrogenation and dehydration on carbon nanotubes: active sites and basic reaction kinetics

Carbon nanotubes were applied for the first time to the methanol conversion reaction showing the advantage of low  $\text{CO}_2$  selectivity and long term stability. The active sites and kinetics for both dehydration and oxidative dehydrogenation reactions were revealed via chemical titration, model catalysts and structure-activity analysis.

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**SrTiO<sub>3</sub> doped with Ru, H<sub>2</sub>-reduced SrTiO<sub>3</sub> doped with Ru and SrTiO<sub>3</sub> codoped with Ru and Sb were developed as active photocatalysts for sacrificial H<sub>2</sub> and O<sub>2</sub> evolution under visible light irradiation. H<sub>2</sub>-Reduced SrTiO<sub>3</sub>:Ru showed the highest activity responding up to 750 nm, almost the whole range of visible light.**

Photocatalytic water splitting is a promising chemical reaction to convert solar energy into storable chemical energy, so-called artificial photosynthesis.<sup>1–6</sup> Utilization of visible light is a key issue to achieve highly efficient solar energy conversion. Accordingly, development of photocatalysts with responses to a wide range of visible light is an important research topic.

Doping of metal ions is a useful technique to make materials responsive to light with longer wavelengths.<sup>2,7</sup> The doped metal ions form impurity levels in the forbidden band of the host material, and hence new energy gaps appear in addition to the band gap of the host material. For example, Rh-doped SrTiO<sub>3</sub> is an established photocatalyst which is highly active for sacrificial H<sub>2</sub> evolution under visible light irradiation.<sup>8</sup> In addition to Rh ions, Cr, Ir, and Ni ions are known as effective dopants.<sup>9–13</sup> We have preliminarily reported that Ru-doped SrTiO<sub>3</sub> shows photocatalytic activities for sacrificial H<sub>2</sub> and O<sub>2</sub> evolution under visible light irradiation.<sup>8</sup> However, the details of the photocatalytic properties and the band structure have not been clarified yet. It is important to improve the Ru-doped SrTiO<sub>3</sub> by some modifications.

Codoping with a second dopant can control the oxidation number of the main dopant. For example, Rh ions are mainly

## Long wavelength visible light-responsive SrTiO<sub>3</sub> photocatalysts doped with valence-controlled Ru for sacrificial H<sub>2</sub> and O<sub>2</sub> evolution†

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doped as Rh<sup>4+</sup> at Ti<sup>4+</sup> sites when only Rh is doped into SrTiO<sub>3</sub>.<sup>14</sup> In contrast, the oxidation number of the rhodium species is controlled from Rh<sup>4+</sup> to Rh<sup>3+</sup> by codoping of Sb<sup>5+</sup> into SrTiO<sub>3</sub> to maintain the charge balance, according to 2Ti<sup>4+</sup> = Rh<sup>3+</sup> + Sb<sup>5+</sup>.<sup>15,16</sup> As a result, Rh,Sb-codoped SrTiO<sub>3</sub> shows activity for water splitting under visible light irradiation,<sup>16</sup> being different from Rh-doped SrTiO<sub>3</sub>. Thus, the oxidation number of the doped metal ions drastically affects the photocatalytic properties.

In the present study, we investigated the photocatalytic properties of Ru-doped SrTiO<sub>3</sub> to develop and improve a photocatalyst responding to long wavelength visible light. Sb-Codoping and H<sub>2</sub>-reduction were applied to Ru-doped SrTiO<sub>3</sub> to control the oxidation number of doped Ru. The band structures of Ru-doped SrTiO<sub>3</sub>, Ru,Sb-codoped SrTiO<sub>3</sub>, and Ru-doped SrTiO<sub>3</sub> after H<sub>2</sub> reduction were also discussed.

Metal ion-doped SrTiO<sub>3</sub> was prepared by a solid-state reaction. The starting materials SrCO<sub>3</sub> (Kanto Chemical, 99.9%), TiO<sub>2</sub> (Soekawa Chemical, 99.9%), RuO<sub>2</sub> (Rare Metallic, 99.9%), Sb<sub>2</sub>O<sub>5</sub> (Nakarai Tesque, 98%), Nb<sub>2</sub>O<sub>5</sub> (Kojundo Chemical, 99.99%) and Ta<sub>2</sub>O<sub>5</sub> (Rare Metallic, 99.99%) were mixed in atomic ratios of Sr/Ti/Ru = 1.015:0.997:0.003 for Ru(0.3%)-doped SrTiO<sub>3</sub>, Sr/Ti/Ru/Sb = 1.015:0.9925:0.003:0.0045 for Ru(0.3%),Sb(0.45%)-codoped SrTiO<sub>3</sub>, and Sr/Ti/Ru/M = 1.015:0.991 - x:0.003:0.006 for Ru(0.3%),Nb(0.6%)- and Ru(0.3%),Ta(0.6%)-codoped SrTiO<sub>3</sub>. The mixture was calcined in an alumina crucible at 1273 K for 10 h. H<sub>2</sub>-Reduced SrTiO<sub>3</sub> doped with Ru was prepared by reduction in one atmosphere of H<sub>2</sub> at 473 K or 673 K for 2 h. The crystal phase of the prepared powder was analyzed on an X-ray diffractometer (Rigaku, MiniFlex) using CuKα radiation. Diffuse reflectance spectra were obtained using a UV-vis-NIR spectrometer (JASCO, Ubest-570) equipped with an integrating sphere and were converted from reflection to K-M function by the Kubelka-Munk method. Electron spin resonance (ESR) spectra were recorded at 77 K on an ESR spectrometer (JEOL, JES-FA200).

Photocatalytic reactions of sacrificial H<sub>2</sub> and O<sub>2</sub> evolution were carried out using a gas-tight circulation system with a

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top-irradiation cell with a Pyrex window. Photocatalyst powder (0.2 g) was dispersed in an aqueous solution (120 mL) containing 10 vol% methanol as a hole scavenger and a certain amount of  $\text{H}_2\text{PtCl}_6$  as a source of a Pt cocatalyst for sacrificial  $\text{H}_2$  evolution. Photocatalyst powder (0.2 g) was dispersed in an aqueous solution (120 mL) containing 20  $\text{mmol L}^{-1}$   $\text{AgNO}_3$  as an electron scavenger for sacrificial  $\text{O}_2$  evolution. The suspension was irradiated with visible light using a 300 W Xe lamp (PerkinElmer, Cermax PE300BF) with a long-pass filter (HOYA L42). The amounts of evolved gases were determined using an online gas chromatograph (Shimadzu, GC-8A, MS-5A column, TCD, Ar carrier). The apparent quantum yield (AQY) for the sacrificial  $\text{O}_2$  evolution was estimated using the following equation.

$$\begin{aligned} [\text{AQY}\%] &= 100 \times \frac{[\text{the number of reacted holes}]}{[\text{the number of incident photons}]} \\ &= 100 \times \frac{[\text{the number of evolved } \text{O}_2 \text{ molecules}] \times 4}{[\text{the number of incident photons}]} \end{aligned}$$

The photon flux of the monochromatic light through the band-pass filters (Asahi Spectra, MAX-303) was measured using a silicon diode head (Ophir Optronics, PD300-UV head and NOVA display).

XRD measurements revealed that Ru(0.3%)-doped  $\text{SrTiO}_3$  ( $\text{SrTiO}_3\text{:Ru}$ ) was obtained without noticeable impurities (Fig. S1<sup>†</sup>), indicating that Ru ions were doped into the  $\text{SrTiO}_3$  lattice. Judging from the ionic radii of  $\text{Ru}^{3+}$  (68 pm, 6 coordination) and  $\text{Ru}^{4+}$  (62 pm, 6 coordination) compared to that of  $\text{Ti}^{4+}$  (60.5 pm, 6 coordination),<sup>17</sup> the Ru ions should be doped at  $\text{Ti}^{4+}$  sites. In the ESR measurements, no signal was observed for non-doped  $\text{SrTiO}_3$ , while Ru-doped  $\text{SrTiO}_3$  gave a small signal, as shown in Fig. 1. The intensity of the signal increased by  $\text{H}_2$ -reduction and Sb-codoping, indicating that the observed ESR signal was from either  $\text{Ti}^{3+}$  or  $\text{Ru}^{3+}$ . Upon considering the stability of  $\text{SrTiO}_3$ ,  $\text{Ti}^{3+}$  may not be formed by  $\text{H}_2$  reduction at 673 K. Thus, we can conclude that Ru was mainly doped as  $\text{Ru}^{4+}$  which is ESR inactive and was reduced to  $\text{Ru}^{3+}$  by  $\text{H}_2$ -reduction and Sb-codoping.

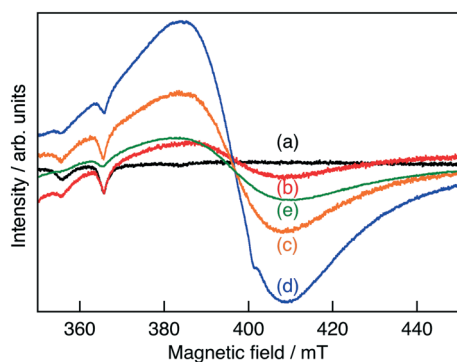


Fig. 1 ESR spectra for  $\text{Ru}^{3+}$  in (a) non-doped  $\text{SrTiO}_3$ , (b)  $\text{SrTiO}_3\text{:Ru}(0.3\%)$ ,  $\text{SrTiO}_3\text{:Ru}(0.3\%)$  after  $\text{H}_2$ -reduction at (c) 473 K and (d) 673 K and (e)  $\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Sb}(0.45\%)$ .

The change in the oxidation number of a dopant, especially a transition metal cation with  $d^n$  configuration ( $n = 1-9$ ), usually affects the photoabsorption properties of the material, as observed for Rh-doped  $\text{SrTiO}_3$  and Ir-doped  $\text{SrTiO}_3$ .<sup>13-16</sup>  $\text{SrTiO}_3\text{:Ru}$  possessed a wide absorption band in the visible light region in addition to the band gap absorption of the  $\text{SrTiO}_3$  host (Fig. 2b). Upon reduction with  $\text{H}_2$ , the absorption at around 500–700 nm increased, while the absorption at around 400–450 nm decreased (Fig. 2c and d). On the basis of the change in the absorption profile, the absorption bands at around 500–700 nm and 400–450 nm were assigned to  $\text{Ru}^{3+}$ - and  $\text{Ru}^{4+}$ -related transitions, respectively. This behavior corresponded to the change in ESR signals.

Sb, Nb and Ta ions were codoped with Ru into  $\text{SrTiO}_3$  to control the Ru to be trivalent. The XRD patterns of Ru,Sb-, Ru,Nb- and Ru,Ta-codoped  $\text{SrTiO}_3$  were the same as that of  $\text{SrTiO}_3\text{:Ru}$  (Fig. S1<sup>†</sup>), indicating the successful doping of Sb, Nb and Ta. Upon codoping with Sb ions, the absorption in the diffuse reflectance spectrum at around 500–800 nm increased, whereas the absorption at around 400–450 nm decreased (Fig. 2e). This is because the doped Ru ions were controlled to be trivalent by codoping with Sb ions. In more detail, two  $\text{Ti}^{4+}$  ions were substituted with  $\text{Ru}^{3+}$  and  $\text{Sb}^{5+}$  ions to maintain the charge balance, according to  $2\text{Ti}^{4+} = \text{Ru}^{3+} + \text{Sb}^{5+}$ . Actually, the intensity of the ESR signal also increased by codoping with Sb ions (Fig. 1e). However, the intensities of the absorption at around 500–800 nm in the diffuse reflectance spectra and the ESR signal were lower than those of the sample after  $\text{H}_2$ -reduction. These lower intensities indicate that  $\text{Ru}^{4+}$  ions still existed even in Ru,Sb-codoped  $\text{SrTiO}_3$ . The profile of the diffuse reflectance spectrum of  $\text{SrTiO}_3\text{:Ru}$  did not change upon codoping of either Nb or Ta ions (Fig. 2f and g). This indicates that the Nb and Ta ions do not contribute to control of the oxidation number of the doped Ru ions, being different from Sb ions. The codopants should locate close to the Ru ions to maintain the charge balance. Both  $\text{Ru}^{3+}$  (68 pm, 6 coordination) of the dopant and  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$  (64 pm, 6 coordination) of the codopants

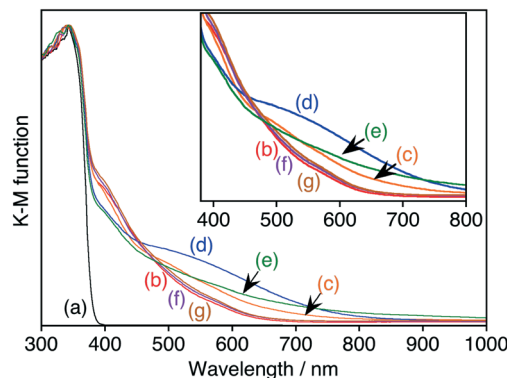


Fig. 2 Diffuse reflectance spectra of (a) non-doped  $\text{SrTiO}_3$ , (b)  $\text{SrTiO}_3\text{:Ru}(0.3\%)$ ,  $\text{SrTiO}_3\text{:Ru}(0.3\%)$  after  $\text{H}_2$ -reduction at (c) 473 K and (d) 673 K, (e)  $\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Sb}(0.45\%)$ , (f)  $\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Nb}(0.6\%)$ , and (g)  $\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Ta}(0.6\%)$ .



possess larger ionic radii than  $\text{Ti}^{4+}$  (60.5 pm, 6 coordination). Therefore, it is unfavourable that  $\text{Ru}^{3+}$  and  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$  are closely located to each other. In contrast,  $\text{Sb}^{5+}$  (60 pm, 6 coordination) possesses a slightly smaller ionic radius than  $\text{Ti}^{4+}$  (60.5 pm, 6 coordination). This suggests that  $\text{Sb}^{5+}$  can locate closely to Ru ions resulting in control of the oxidation number of the doped Ru ions compared to Nb and Ta ions.

Table 1 shows the photocatalytic activities for sacrificial  $\text{H}_2$  and  $\text{O}_2$  evolution over  $\text{SrTiO}_3\text{:Ru}$ ,  $\text{H}_2$ -reduced  $\text{SrTiO}_3\text{:Ru}$  and codoped  $\text{SrTiO}_3\text{:Ru}$  under visible light irradiation.  $\text{SrTiO}_3\text{:Ru}$  showed activities for both sacrificial  $\text{H}_2$  evolution and  $\text{O}_2$  evolution, as previously reported.<sup>8</sup>  $\text{H}_2$ -Reduced  $\text{SrTiO}_3\text{:Ru}$  showed a higher activity for the sacrificial  $\text{O}_2$  evolution than the pristine  $\text{SrTiO}_3\text{:Ru}$  and the activity increased with increasing temperature of  $\text{H}_2$  reduction.

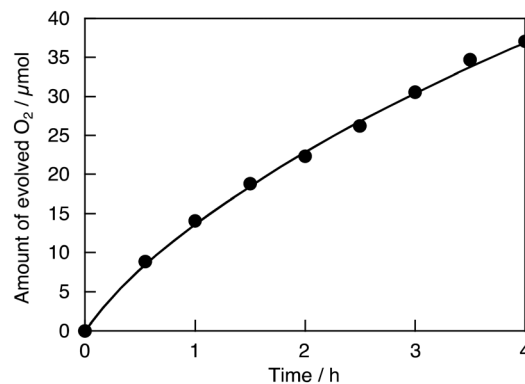
In contrast, the activity for the sacrificial  $\text{H}_2$  evolution was decreased by  $\text{H}_2$  reduction. The  $\text{H}_2$ -reduced  $\text{SrTiO}_3\text{:Ru}$  continuously produced  $\text{O}_2$  under visible light irradiation, as shown in Fig. 3. The turnover number which is the ratio of the number of reacted holes to the number of doped Ru ions is calculated to be 45 using the amount of evolved  $\text{O}_2$  (37  $\mu\text{mol}$  for 4 h) and doped Ru ions (3.3  $\mu\text{mol}$  in 0.2 g of  $\text{SrTiO}_3\text{:Ru}$ ). The activity for sacrificial  $\text{O}_2$  evolution over Ru,Sb-codoped  $\text{SrTiO}_3$  was also higher than that over  $\text{SrTiO}_3\text{:Ru}$ , while the activity for sacrificial  $\text{H}_2$  evolution was lower. This trade-off between the sacrificial  $\text{H}_2$  evolution and  $\text{O}_2$  evolution for the codoped photocatalyst was similar to that for Rh,Sb-codoped  $\text{SrTiO}_3$ .<sup>15,16</sup> A doped photocatalyst with impurity levels formed by a dopant with an oxidation number stabilized by  $\text{H}_2$ -reduction and Sb-codoping is sometimes not suitable for  $\text{H}_2$  evolution, as observed for Rh,Sb-codoped  $\text{SrTiO}_3$ .<sup>15,16</sup> Ru,Nb- and Ru,Ta-codoped  $\text{SrTiO}_3$  showed similar activities for sacrificial  $\text{H}_2$  and  $\text{O}_2$  evolution to that of  $\text{SrTiO}_3\text{:Ru}$ . Thus, the activity for sacrificial  $\text{O}_2$  evolution increased upon increasing the rate of doped  $\text{Ru}^{3+}$  by  $\text{H}_2$  reduction and Sb-codoping.

To further understand the relationship between the doped  $\text{Ru}^{3+}$  ions and the activity for  $\text{O}_2$  evolution, action spectra were measured, as shown in Fig. 4.  $\text{SrTiO}_3\text{:Ru}$ ,  $\text{H}_2$ -reduced  $\text{SrTiO}_3\text{:Ru}$  and Ru,Sb-codoped  $\text{SrTiO}_3$  ( $\text{SrTiO}_3\text{:Ru,Sb}$ ) showed activity for sacrificial  $\text{O}_2$  evolution using light up to 660 nm

**Table 1** Sacrificial  $\text{H}_2$  and  $\text{O}_2$  evolution over the  $\text{SrTiO}_3\text{:Ru}$ ,  $\text{H}_2$ -reduced  $\text{SrTiO}_3\text{:Ru}$  and codoped  $\text{SrTiO}_3\text{:Ru}$  photocatalysts under visible light irradiation

Photocatalyst <sup>a</sup>	Activity/ $\mu\text{mol h}^{-1}$	
	$\text{H}_2$ <sup>b</sup>	$\text{O}_2$ <sup>c</sup>
$\text{SrTiO}_3\text{:Ru}(0.3\%)$	4.0	4.4
$\text{SrTiO}_3\text{:Ru}(0.3\%)$ with $\text{H}_2$ -red. (473 K)	1.7	8.0
$\text{SrTiO}_3\text{:Ru}(0.3\%)$ with $\text{H}_2$ -red. (673 K)	1.8	16.1
$\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Sb}(0.45\%)$	0.2	7.3
$\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Nb}(0.6\%)$	3.3	3.3
$\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Ta}(0.6\%)$	2.4	4.3

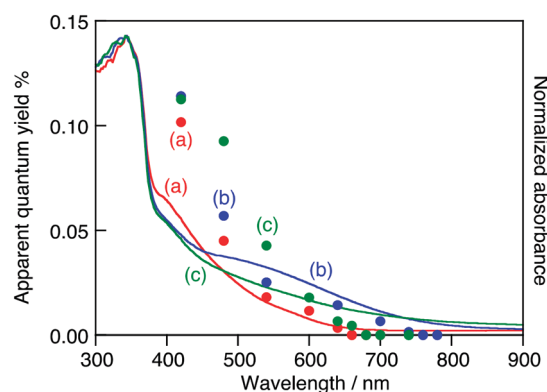
Photocatalyst: 0.2 g; reactant solution: 120 mL; light source: 300 W Xe lamp with a long-pass filter ( $\lambda > 420$  nm, L42).<sup>a</sup> Prepared at 1273 K for 10 h by a solid-state reaction with 1.5 at% excess Sr. <sup>b</sup> Pt(0.3 wt%)-Cocatalyst; 10 vol% MeOH aq. <sup>c</sup> 20 mmol  $\text{L}^{-1}$   $\text{AgNO}_3$  aq.



**Fig. 3** Photocatalytic  $\text{O}_2$  evolution over  $\text{SrTiO}_3\text{:Ru}(0.3\%)$  after  $\text{H}_2$ -reduction at 673 K from an aqueous  $\text{AgNO}_3$  solution under visible light irradiation. Photocatalyst: 0.2 g; reactant solution: 20 mmol  $\text{L}^{-1}$   $\text{AgNO}_3$  aq., 120 mL; light source: 300 W Xe lamp with a long-pass filter ( $\lambda > 420$  nm, L42).

(1.88 eV), 750 nm (1.65 eV) and 670 nm (1.85 eV), respectively.

The onset of the action spectrum for the  $\text{O}_2$  evolution over the  $\text{SrTiO}_3\text{:Ru}$  in which doped Ru was mainly tetravalent was similar to that of the photoanodic current of an  $\text{RuO}_2$ -doped  $\text{SrTiO}_3$  photoelectrode, though the condition of the doped Ru was not clear for the photoelectrode.<sup>18</sup> As discussed above, the corresponding absorption bands were assigned to  $\text{Ru}^{3+}$ -related transitions. The possible band structures of  $\text{SrTiO}_3\text{:Ru}$ ,  $\text{H}_2$ -reduced  $\text{SrTiO}_3\text{:Ru}$  and  $\text{SrTiO}_3\text{:Ru,Sb}$  judging from the action spectra are summarized in Fig. 5. The valence band maximum consisting of the O2p orbitals of metal oxides is generally located at around +3.0 V vs. NHE at pH 0,<sup>19</sup> and the band levels of metal oxides shift with  $-0.059$  V  $\text{pH}^{-1}$ . Accordingly, the conduction band minimum and the valence band maximum of  $\text{SrTiO}_3$  with a band gap of 3.2 eV are estimated to be at  $-0.61$  V and  $+2.59$  V vs. NHE at pH 7, respectively. When the  $\text{Ru}^{3+}$ -related transition is the



**Fig. 4** Action spectra for photocatalytic  $\text{O}_2$  evolution from an aqueous  $\text{AgNO}_3$  solution (closed circles) and diffuse reflectance spectra (solid lines) of (a)  $\text{SrTiO}_3\text{:Ru}(0.3\%)$ , (b)  $\text{SrTiO}_3\text{:Ru}(0.3\%)$  after  $\text{H}_2$ -reduction at 673 K and (c)  $\text{SrTiO}_3\text{:Ru}(0.3\%),\text{Sb}(0.45\%)$ . Photocatalyst: 0.2 g; reactant solution: 20 mmol  $\text{L}^{-1}$   $\text{AgNO}_3$  aq., 120 mL; light source: 300 W Xe lamp with a band-pass filter; cell: top-irradiation cell with a Pyrex window.



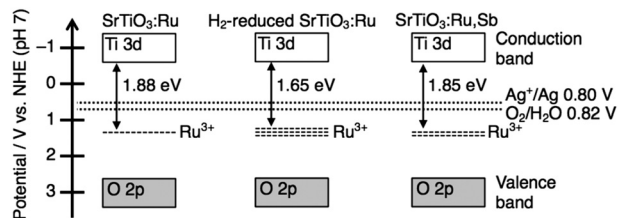


Fig. 5 Proposed band structures of SrTiO<sub>3</sub>:Ru, H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru and SrTiO<sub>3</sub>:Ru,Sb.

excitation of electrons from impurity levels formed by Ru<sup>3+</sup> to the conduction band formed by Ti3d, the potential of impurity levels formed by Ru<sup>3+</sup> are estimated to be +1.04 V–+1.27 V vs. NHE at pH 7. The redox potential of Ag<sup>+</sup>/Ag and H<sub>2</sub>O/O<sub>2</sub> are +0.80 V and +0.82 V vs. NHE at pH 7, respectively. Thus, photogenerated electrons in the conduction band and holes at the impurity levels possess thermodynamically enough potential to reduce Ag<sup>+</sup> to Ag and oxidize H<sub>2</sub>O to O<sub>2</sub>, respectively. In contrast to this, assuming that the Ru<sup>3+</sup>-related transition is the excitation of electrons from the valence band formed by O2p to the impurity levels formed by Ru<sup>3+</sup>, the potential of the impurity levels are estimated to be +0.71–+0.94 V vs. NHE at pH 7.

These potentials are insufficient to reduce Ag<sup>+</sup> to Ag (+0.80 V vs. NHE). Thus, we can conclude that the sacrificial O<sub>2</sub> evolution from an aqueous AgNO<sub>3</sub> solution proceeded by the excitation from the impurity levels formed by Ru<sup>3+</sup> to the conduction band of SrTiO<sub>3</sub>. Although the impurity levels are formed by Ru<sup>4+</sup>, the Ru<sup>4+</sup>-related absorption does not contribute to the photocatalytic reactions, judging from the action spectra shown in Fig. 4. Sb<sup>5+</sup> does not form impurity levels in the forbidden band of SrTiO<sub>3</sub>. Thus, the impurity levels formed by Ru<sup>4+</sup> and Sb<sup>5+</sup> are not described in Fig. 4 to simplify the band structure relating the photocatalytic reactions.

SrTiO<sub>3</sub>:Ru,Sb showed higher apparent quantum yields than H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru under light irradiation at around 500 nm, while the former showed lower apparent quantum yields than the latter under light irradiation at around 650 nm, as shown in Fig. 4. The doped Ru was controlled to become Ru<sup>3+</sup> by both H<sub>2</sub>-reduction and Sb-codoping. The advantage of the Sb-codoping at Ti<sup>4+</sup> sites is the self-charge compensation due to the formation of Sb<sup>3+</sup> with an excess amount of Sb<sub>2</sub>O<sub>5</sub> in the starting material.<sup>9</sup> The excessively doped antimony was doped as Sb<sup>3+</sup> and Sb<sup>5+</sup> at Ti<sup>4+</sup> to maintain the charge balance, according to 2Ti<sup>4+</sup> = Sb<sup>3+</sup> + Sb<sup>5+</sup>. In contrast, oxygen vacancies were formed by H<sub>2</sub>-reduction. Therefore, SrTiO<sub>3</sub>:Ru,Sb should basically show higher apparent quantum yields than H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru because of less defects. However, the H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru possessed a narrower energy gap than SrTiO<sub>3</sub>:Ru,Sb resulting in absorption of more photons. Therefore, the H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru showed higher apparent quantum yields than SrTiO<sub>3</sub>:Ru,Sb at wavelengths close to the absorption edge of H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru at around 650 nm.

There is a negative correlation between the order of the energy gap (SrTiO<sub>3</sub>:Ru > SrTiO<sub>3</sub>:Ru,Sb > H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru) and the order of the rate of Ru<sup>3+</sup> ions (SrTiO<sub>3</sub>:Ru < SrTiO<sub>3</sub>:Ru,Sb < H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru) judging from the ESR spectra (Fig. 1). When the rate of Ru<sup>3+</sup> increases, the impurity levels formed by Ru<sup>3+</sup> become wide due to the increased density of states. Accordingly, the energy gap between the conduction band and the impurity levels formed by Ru<sup>3+</sup> becomes narrow, as shown in Fig. 5. The widened impurity levels are also considered to be favorable for migration of photogenerated holes. Thus, the possible reasons why H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru showed higher activity for the sacrificial O<sub>2</sub> evolution than SrTiO<sub>3</sub>:Ru and SrTiO<sub>3</sub>:Ru,Sb are the longest response wavelength and favorable impurity levels for hole migration.

## Conclusions

In conclusion, the SrTiO<sub>3</sub>:Ru,Sb and H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru photocatalysts as well as SrTiO<sub>3</sub>:Ru showed activities for sacrificial H<sub>2</sub> and O<sub>2</sub> evolution under visible light irradiation. Ru ions were mainly doped as tetravalent Ru in SrTiO<sub>3</sub>:Ru and the Ru<sup>4+</sup> ions became Ru<sup>3+</sup> ions by Sb-codoping and H<sub>2</sub>-reduction. The H<sub>2</sub> evolution activity decreased by controlling Ru to become trivalent, while the O<sub>2</sub> evolution activity increased. Photocatalytic reactions over SrTiO<sub>3</sub>:Ru, SrTiO<sub>3</sub>:Ru,Sb and H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru proceeded by the excitation from the impurity levels formed by Ru<sup>3+</sup> to the conduction band of SrTiO<sub>3</sub>. Among them, H<sub>2</sub>-reduced SrTiO<sub>3</sub>:Ru especially showed the highest O<sub>2</sub> evolution activity and the longest response wavelength up to 750 nm, because of widening of the impurity level formed by Ru<sup>3+</sup>. Thus, we successfully developed metal oxide photocatalysts with a response to long wavelength visible light (near infrared) by Ru<sup>3+</sup> doping. This responsive wavelength is almost the longest among those of photocatalysts which are active for O<sub>2</sub> evolution. Thus, Ru-doping will be one strategy to develop metal oxide photocatalysts responding to a wide range of visible light. Moreover, these photocatalysts can be employed as O<sub>2</sub>-evolving photocatalysts in a Z-scheme photocatalyst system.

## Conflicts of interest

There are no conflicts to declare.

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